Polymerisable compositions for making transparent polymer substrates, resulting transparent polymer substrates and uses thereof in optics

The present invention relates to the field of compositions of polymerisable monomers which, after polymerisation, give transparent polymer substrates, and to their use for making optical, particularly ophthalmic, lenses.

Optical lenses for ophthalmic use made from organic polymer materials are known and have been used for many years.

One of the most widely used materials is obtained by polymerisation of compositions containing diethylene glycol diallyl carbonate (subsequently referred to as CAD).

This monomer is commercially available, for example under the trade name CR39®.

An example of a commercial ophthalmic lens in a material of this type is the ORMA® lens.

This material has intrinsically good mechanical properties, in particular impact strength and scratch resistance, as well as good resistance to organic solvents.

This material may also be readily coloured when desired by the customer.

One of the disadvantages of the use of CAD is the fact that the polymerisation of this monomer is essentially performed thermally, with particularly long heat cycles (several hours or even days).

It would thus be desirable to reduce the length of these polymerisation cycles so as, amongst other reasons, to be able to respond to customers as quickly as possible, to limit the length of time that the moulds used for the lens production are in use, and to reduce the manufacturing costs.

In addition, although CAD materials are generally satisfactory, it would also be desirable to produce materials with improved intrinsic properties.

Various types of materials have already been proposed in the prior art.

The patent US-A-4138538 discloses compositions of allyl monomers such as CAD, containing a methacrylic monomer such as a polyethylene glycol di(meth)acrylate.

This methacrylic monomer may be used at a concentration of 20 to 70% by weight of the polymerisable mixture.

The mixture is photopolymerised, preferably at low temperature, then a thermal treatment is performed.

The patent US-A-4650845 discloses monomer compositions comprising from 0 to 100 parts by weight of a first component which is a poly(meth)acrylate urethane monomer, and from 100 to 0 parts by weight of a second component which is a composition containing :

A) from 30 to 60% by weight of a polyacrylate monomer,

B) from 20 to 70% by weight of a modifier of the shrinkage during the polymerisation,

C) from 0 to 30% by weight of a diluent monomer.

The compositions are preferably photopolymerised.

In practice, the compositions disclosed generally lead to highly crosslinked polymers due to the presence of monomers containing multiple functional groups.

The compositions generally contain monomers containing at least 4 (meth)acrylate groups.

The patent US-A-4912185 discloses compositions of polymerisable monomers, for the production of ophthalmic lenses or video discs, comprising at least one polyoxyalkylene glycol acrylate or methacrylate monomer, at least one crosslinking agent containing several unsaturated functions and at least one urethane monomer with 2 to 6 methacrylic end groups.

In practice, the crosslinking agent cited above contains 3 to 4 vinyl, acrylic or methacrylic functional groups.

Such compositions are preferably hardened by mixed UV/thermal polymerisation.

The patent EP-A-453149 discloses compositions containing a polyoxyalkylene glycol di(meth)acrylate monomer; a monomer containing a bisphenol A unit and leading, by homopolymerisation, to a polymer with refractive index greater than 1.55 and a urethane monomer with 2 to 6 (meth)acrylic end groups.

The polymerisation is preferably mixed UV/thermal.

The patent US-A-5183870 discloses compositions comprising from 10 to 60% by weight of a polybutylene glycol di(meth)acrylate, from 20 to 80% by weight of a poly(meth)acrylate urethane, from 5 to 60% by weight of a specific mono(meth)acrylate monomer and from 0 to 60% by weight of a compound having at least one polymerisable double bond.

According to the patent US-A-5183870, the choice of the polybutylene glycol di(meth)acrylate is essential to achieve a good compromise between impact strength and low water absorption properties.

Comparative example 7 discloses a composition containing a polyethylene glycol di(meth)acrylate, a dimethacrylate urethane and a tricyclo[5.2.1.0^{2,6}]decan-8-yl methacrylate.

The polymer resulting from this composition has a high water absorption level of 3.6%.

The patent US-A-5880171 discloses photopolymerisable compositions containing :

from 20 to 90%, and preferably at least 50% by weight of an epoxy or polyester urethane oligomer with (meth)acrylate end groups and 5 to 80% by weight of an optional diluent which is a hydrocarbon diol ester with (meth)acrylate and/or tri, tetra or poly(meth)acrylate end groups.

The patent US-A-5566027 discloses photopolymerisable compositions comprising from 25 to 45% of a polyester urethane oligomer containing several (meth)acrylic groups linked to a polyester oligomer via a urethane group and having a molecular weight of at least 700, from 31 to 70% by weight of a polyfunctional (meth)acrylate with an average molecular weight of at least 700 and from 5 to 55% by weight of a monofunctional (meth)acrylate.

This composition is used as a varnish applied to ophthalmic lenses.

There is no provision for the use of a composition of this type to produce the body of the lens.

Thus it can be seen that many polymerisable compositions leading to materials with refractive index of the order of 1.5 have been proposed in the prior art, without however giving complete satisfaction for producing transparent polymer substrates usable in the optics field.

A first object of the present invention is thus to provide new compositions of polymerisable monomers leading to transparent polymer substrates able to be substituted for CAD-based polymers, in other words with properties which are overall similar to those of CAD, and preferably better.

The optical substrates must in particular have all the following properties:

- high transparency (transmission generally greater than 85%, and preferably greater than or equal to 90%), with an absence of, or only very slight, diffusion of the light,

- low density, less than 1.4, preferably less than 1.3 and even better less than 1.2,

- refractive index between 1.48 and 1.52,

- high Abbe number, greater than or equal to 40, preferably greater than or equal to 45 and even better greater than or equal to 50, so as to avoid chromatic aberrations,

- absence of colour after polymerisation, in particular a low yellow index and an absence of yellowing over time,

- good impact strength (in particular an uncoated lens should preferably pass the FDA ball dropping test),

- good resistance to static stresses,

- good scratch resistance,

- good suitability for accepting different treatments (deposit of hard, anti-reflection, primary anti-shock coatings, etc.), and particular good suitability for coloration,

- good suitability for surface and edge finishing treatments, without the overall geometry of the lens being distorted during such operations,

- low water absorption level.

The polymer substrates according to the invention have a water absorption level which is preferably less than 1.5% and more preferably less than 1%.

A second object of the invention is to provide compositions which may be readily and rapidly polymerised, in particular by photopolymerisation or by mixed photo- and thermal polymerisation techniques, so as to reduce the length of the lens production cycle.

The composition of the polymerisable monomers according to the invention comprises :
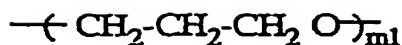
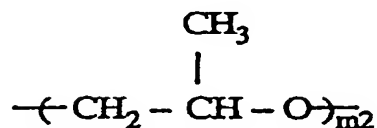- 40 to 95 parts by weight of one or more monomers (I) of formula :

$$CH_2 = \underset{\underset{O}{\|}}{\overset{\overset{R_1}{|}}{C}} - C - O - A - \underset{\underset{O}{\|}}{\overset{\overset{R_2}{|}}{C}} - C = CH_2$$
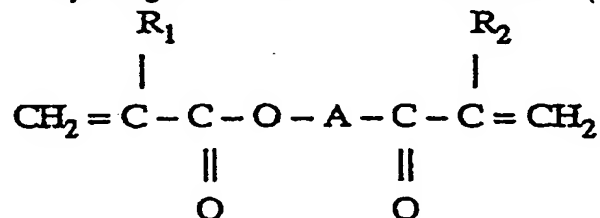
in which

R_1 and R_2 represent H or CH_3,

A represents a divalent radical of formula

$$-\!\!+\!CH_2\text{-}CH_2\text{-}CH_2 \; O\!\!+\!\!\!_{m1}$$

or

$$\begin{array}{c} CH_3 \\ | \\ -\!\!+\!CH_2 - CH - O\!\!+\!\!\!_{m2} \end{array}$$

m_1 and m_2 are each integers varying from 2 to 6, and

- 5 to 50 parts by weight of a monomer (II) comprising at least one urethane unit and at least two (meth)acrylate functions.

The composition of monomers according to the invention generally has a viscosity less than or equal to 0.3 Pa.s, preferably less than 0.2 Pa.s.

The first important component of the compositions according to the invention is the monomer or monomers (I) corresponding to the formula above.

More exactly, it consists of (meth)acrylic esters of propylene glycol containing a central radical A, which may be linear or branched, such as defined above.

The first component is a monomer or mixture of monomers (I) with relatively short chain lengths, in other words the number of propylene glycol units present in the radical A must be equal to or less than 6 and preferably between 2 and 6 for each of the monomers (I).

When several monomers (I) are used in a mixture, an average value may be defined :

$$\overline{m} = \sum_{m=2}^{6} X_m \cdot m$$

in which X_m is the ratio by weight of monomer (I) for which A contains m propylene glycol units in its chain compared to the total weight of monomers of formula (I).

When commercially available products which are already mixtures of monomers are used as the first component of the invention, this value $\overline{m}$ may easily be obtained by HPLC analysis of the mixture followed by the calculation

$$X_m = \frac{S_m}{S \; total}$$

where S_m represents the area of the peak corresponding to the monomer (I) containing m propylene glycol units in the divalent radical A, and S represents the total area of all the peaks corresponding to the monomers (I) for which m varies from 2 to 6.

According to the invention, it is preferable to use mixtures of several monomers (I) whose average value $\overline{m}$ as defined above is less than 5 and preferably varies from 2 to 4.

It is also preferable that the monomers (I) have a branched structure, in other words that the radical A represents :

$$-\left(CH_2 - CH - O\right)_{\overline{m2}}$$
$$| \quad CH_3$$
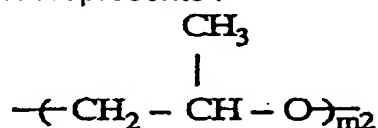
m_2 having the meaning stated previously.

The compositions according to the invention comprise from 50 to 95 parts by weight of monomer (I), the total weight of monomers (I) and (II) representing 100 parts by weight.

It is preferable to use a mixture of several monomers (I) whose central unit A is :

$$-\left(CH_2 - CH - O\right)_{\overline{m2}}$$
$$| \quad CH_3$$
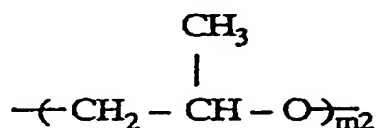
with m_2 being an integer with value from 2 to 6 according to the following mass ratios :

$m_2 = 2$ 27%

$m_2 = 3$ 47%

$m_2 = 4$ 20%

$m_2 = 5$ 4%

$m_2 = 6$ 2%

with an average value $\overline{m_2} = 3.07$.

This mixture will be referred to in the remainder of this application as PPG 200 di(meth)acrylate (or PPG 200 DMA).

In general the first component contributes rigidity to the polymer network comprising the final substrate.

The second component of the compositions according to the invention is a monomer or mixture of monomers (II) comprising at least one urethane unit and at least two (meth)acrylate functions.

Two families of monomers (II) with urethane units are preferably used.

The first family consists of urethane di(meth)acrylate oligomers, and, preferably, those which are aliphatic polyesters.
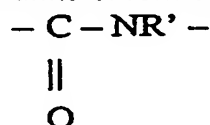
Examples of such compounds are the urethane di(meth)acrylate oligomers from the company Cray Valley, in particular the product known under the trade name CN934®.

The second family consists of monomers (II) with the formula

$$Q \left[W\text{-O} - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle R}{|}}{C} = CH_2 \right]_n$$
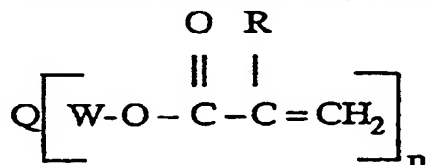
in which Q is a radical of valency n, with linear, branched or cyclic structure, containing at least two units of formula :

$$- \overset{\|}{\underset{O}{C}} - NR' -$$

W is a divalent alkyl radical, with linear or branched structure, with from 1 to 5 carbon atoms.
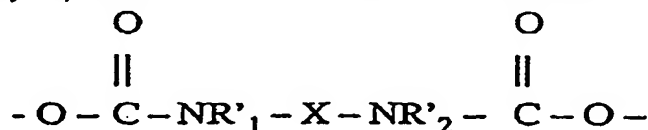
n varies from 2 to 4

R represents H or CH_3-, and

R' represents H or a valence bond

W preferably represents the radical $-CH_2CH_2-$

Q preferably represents a divalent radical of formula :

$$- O - \overset{\overset{\displaystyle O}{\|}}{C} - NR'_1 - X - NR'_2 - \overset{\overset{\displaystyle O}{\|}}{C} - O -$$

in which X represents a linear or branched divalent alkyl chain with from 1 to 15 carbon atoms, preferably 8 to 12 carbon atoms.

R'_1 and R'_2 independently represent H or CH_3.

A monomer of this type is commercially available under the trade name PLEX® 6661-0 and has the formula :

$$CH_2= \overset{\overset{\textstyle H_3C}{|}}{C} - \overset{\overset{\textstyle O}{\|}}{C} - O - CH_2 - CH_2 - O - \quad \overset{\overset{\textstyle O}{\|}}{C} - NH - CH_2 - \overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle R'_3}{|}}{C}} \overset{\overset{\textstyle}{}}{\underset{\underset{\textstyle}{\|}}{C}} CH_2$$

$$CH_2= \overset{\overset{\textstyle H_3C}{|}}{C} - \overset{\overset{\textstyle O}{\|}}{C} - O - CH_2 - CH_2 - O - \overset{\overset{\textstyle O}{\|}}{C} - NH - CH_2 - CH_2 \overset{}{\underset{\underset{\textstyle CH_3}{|}}{C}} - R'_4$$

in which R'$_3$ and R'$_4$ independently represent H or CH$_3$.

Among the second family of monomers (II), other preferred monomers are those in which Q represents a trivalent radical of formula :

5

Monomers of this type which are commercially available have the formula:

in which R"$_1$, R"$_2$ and R"$_3$ independently represent H or CH$_3$.
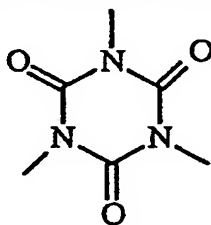
10   The monomer of the above formula in which R"$_1$, R"$_2$ and R"$_3$ each represent a methyl group is available from the company Cray Valley under the trade name SR290.

The monomer of the above formula in which R"$_1$, R"$_2$ and R"$_3$ each represent a hydrogen atom is available from the company Cray Valley under the

15   trade name SR368.

The monomer (II) is present in a proportion of 5 to 50 parts by weight, preferably 10 to 40 parts by weight compared to the total weight of monomers (I) and (II).

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Commercially available monomers include :

1. aliphatic diacrylate urethanes

- CN934, 964, 965, 963, 966, 967, 981 from the company Cray Valley ;

- EBECRYL 230, 244, 245, 270, 284, 285, 4830, 4835, 8800 from the company UCB ;

2. aromatic diacrylate urethanes

- CN970, 972, 973 and 976 from the company Cray Valley ;

- EBECRYL 210, 215, 4244 from the company UCB ;

3. urethane acrylates with functionality ≥ 3

-Triacrylate : CN920, 922, 923, 924, 929 (Cray Valley)

           EBECRYL 204, 205, 254, 264, 265 (UCB)

- Tetracrylate : CN925, 945, 995 (Cray Valley)

           U4HA (SHIN NAKAMURA)

- Hexaacrylate : CN975 (Cray Valley)

           EBECRYL 220, 1290, 2220, 5129 (UCB);

           U6HA (SHINNAKAMURA)

4. aliphatic methacrylate urethanes

- PLEX® 66610 (ROHM) ;

- U4H (tetrafunctional methacrylate from SHIN NAKAMURA).

The monomer compositions according to the invention may include other polymerisable monomers (III) different from monomers (I) and (II), which may integrate into the final network obtained, in particular monomers polymerisable by free radical mechanisms.

These monomers (III) represent from 0 to 30%, preferably 0 to 10% by weight, compared to the total weight of monomers (I) and (II).

These monomers (III) may include the alkyl (meth)acrylates such as methyl (meth)acrylate and ethyl (meth)acrylate, the cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate and dicyclopentyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, the naphthyl (meth)acrylates, the phenoxyalkyl (meth)acrylates such as phenoxyethyl (meth)acrylate and phenoxybutyl (meth)acrylate, the alkylene glycol di(meth)acrylates such as ethylene glycol di(meth)acrylate and propylene glycol di(meth)acrylate, the poly(alkylene) glycol di(meth)acrylates different from the monomers (I) such as poly(ethylene) and poly(butylene) glycol di(meth)acrylates, neopentyl glycol di(meth)acrylate, compounds of bisphenol-A di(meth)acrylates and their mixtures.

The compounds of bisphenol-A di(meth)acrylates include compounds of formula :

$$CH_2=C-C(OCH_2CH_2)_{n_1}-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O(CH_2CH_2O)_{n_2}-C-C=CH_2$$
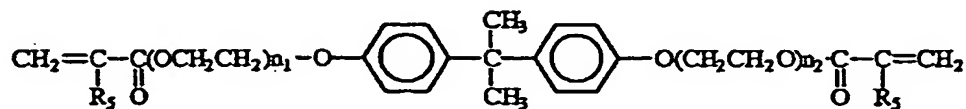
in which R_5 represents H or CH_3 and $n_1 + n_2$ has an average value of from 0 to 40.

Preferred compounds corresponding to the above formula are those for which $R_5 = CH_3$ and $\overline{n_1 + n_2} = 2.6$ (EBADMA), $\overline{n_1 + n_2} = 4$ (DBADMA), $\overline{n_1 + n_2} = 10$ (OBADMA) and $\overline{n_1 + n_2} = 30$.

The monomer (III) may be one monomer or a mixture of monomers corresponding to the chemical structure of monomer (I) and for which m_1 or m_2 is an integer greater than 6, generally from 7 to 20. In this case, the quantity of monomers (III) is such that the mean :
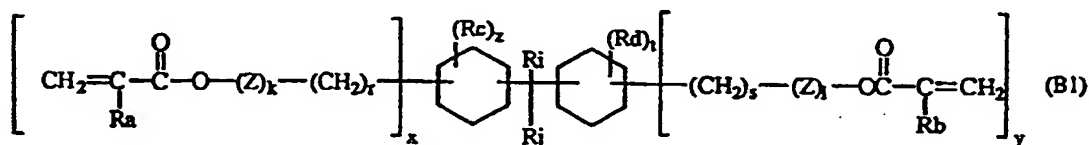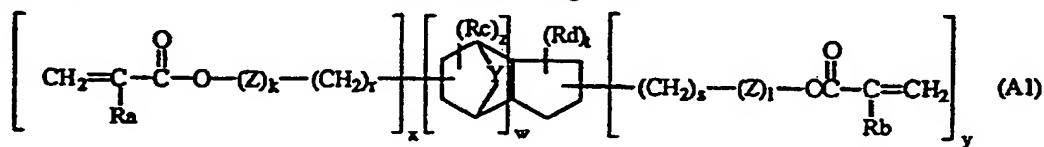
$$\overline{m} = \sum_{m=1}^{20} X_m \cdot m$$
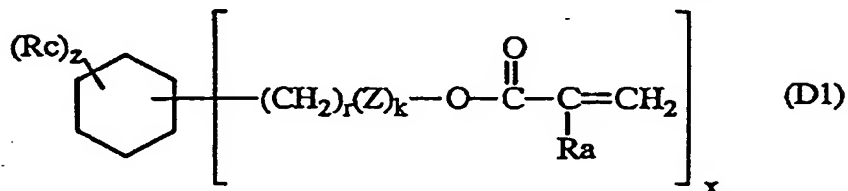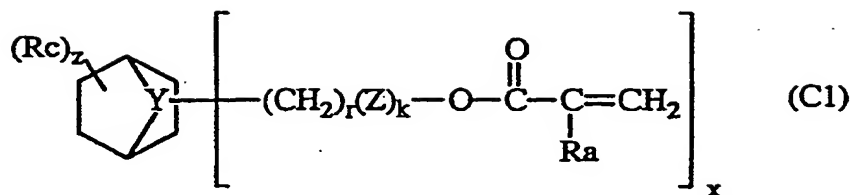
remains less than 5.

The additional monomer (III) may be a monomer with high Abbe number and containing one or more (meth)acrylate functions.

By monomer with high Abbe number should be understood a monomer able to generate, by homopolymerisation, a transparent polymer with high Abbe number, in other words at least 50, and preferably at least 55.

The monomer with high Abbe number preferably contains at least one non-aromatic cyclic or polycyclic hydrocarbon radical.

The monomer (III) with high Abbe number is preferably selected from at least one of the monomers of the following formula :

$$\left[CH_2=\underset{Ra}{\overset{O}{\underset{|}{\overset{||}{C}}}}-C-O-(Z)_k-(CH_2)_r\right]_x\left[\underset{(Rc)_z}{\overset{(Rd)_t}{Y}}\right]_w\left[(CH_2)_s-(Z)_l-O\overset{O}{\overset{||}{C}}-\underset{Rb}{\overset{|}{C}}=CH_2\right]_y \quad (A1)$$

$$\left[CH_2=\underset{Ra}{\overset{O}{\underset{|}{\overset{||}{C}}}}-C-O-(Z)_k-(CH_2)_r\right]_x\left[\underset{(Rc)_z}{\overset{Ri}{\underset{Rj}{}}}(Rd)_t\right]\left[(CH_2)_s-(Z)_l-O\overset{O}{\overset{||}{C}}-\underset{Rb}{\overset{|}{C}}=CH_2\right]_y \quad (B1)$$

$$(Rc)_z \quad \left[-(CH_2)_r(Z)_k - O - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle Ra}{|}}{C} = CH_2 \right]_x \quad (C1)$$

$$(Rc)_z \quad \left[-(CH_2)_r(Z)_k - O - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle Ra}{|}}{C} = CH_2 \right]_x \quad (D1)$$
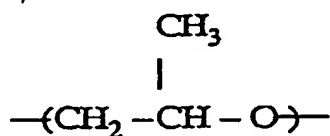
In these formulas :

Y is a divalent radical selected from $-O-$, $-CH_2-$, $-C(CH_3)_2-$, $-C(H)(CH_3)$

Z is a divalent radical selected from $-(CH_2)_p-O-$

p being an integer from 1 to 4, and

$$-(CH_2 - \underset{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{}}}{CH} - O)-$$

R_a, R_b represent H or CH_3

R_c, R_d independently represent a linear or branched alkyl radical with 1 to 6 carbon atoms

R_i, R_j independently represent a linear or branched alkyl radical with 1 to 10 carbon atoms

w is an integer from 1 to 3,

x is an integer from 0 to 3,

y is an integer from 0 to 3,

on condition that $x + y \geq 1$,

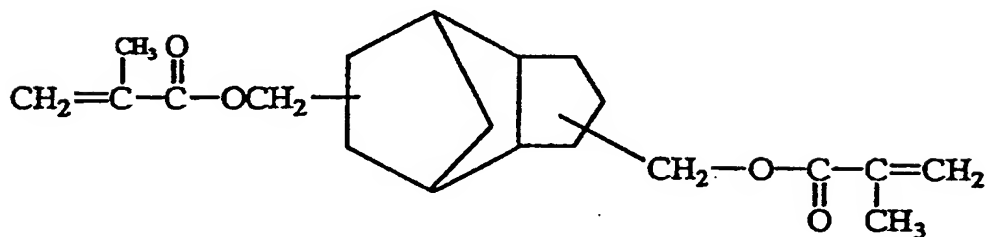k is an integer from 0 to 6,

l is an integer from 0 to 6,

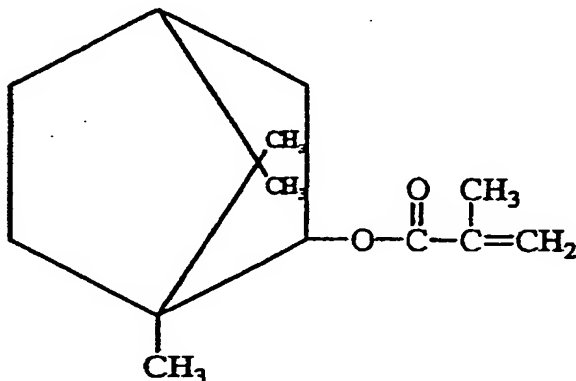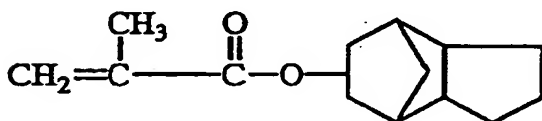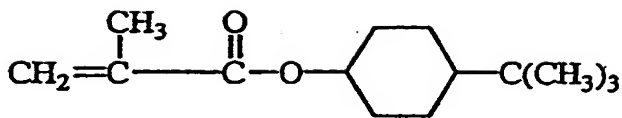r is an integer from 0 to 6,

s is an integer from 0 to 6,

z is an integer from 0 to 3, and

t is an integer from 0 to 3.

The monomers (III) with high Abbe number which are particularly preferred are selected from the monomers of formula :

$$CH_2\!=\!\overset{\overset{\displaystyle CH_3}{|}}{C}\!\!-\!\!\overset{\overset{\displaystyle O}{\parallel}}{C}\!-\!O\!-\!\langle hexyl \rangle\!-\!C(CH_3)_3$$

$$CH_2\!=\!\overset{\overset{\displaystyle CH_3}{|}}{C}\!\!-\!\!\overset{\overset{\displaystyle O}{\parallel}}{C}\!-\!O\!-\!\langle bicyclic \rangle$$

$$\langle ring\ structure \rangle\!-\!O\!-\!\overset{\overset{\displaystyle O}{\parallel}}{C}\!-\!\overset{\overset{\displaystyle CH_3}{|}}{C}\!=\!CH_2$$

$$CH_2\!=\!\overset{\overset{\displaystyle CH_3}{|}}{C}\!-\!\overset{\overset{\displaystyle O}{\parallel}}{C}\!-\!OCH_2\!-\!\langle tricyclic \rangle\!-\!CH_2\!-\!O\!-\!\overset{\underset{\displaystyle O}{\parallel}}{C}\!-\!\overset{\underset{\displaystyle CH_3}{|}}{C}\!=\!CH_2$$

The compositions according to the invention also contain a system for initiating the polymerisation. The system for initiating the polymerisation may comprise one or more agents for initiating thermal or photochemical
5   polymerisation or a mixture of thermal and photochemical initiation agents. These initiators are well known in the state of the art and any conventional initiator may be used. The thermal polymerisation initiators which may be used in the present invention include the peroxides such as benzoyl peroxide, cyclohexyl peroxydicarbonate, and isopropyl peroxydicarbonate.

10   The photoinitiators include in particular 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-1,2-diphenylethan-1-one, and the alkyl benzoyl ethers.

The initiators are in general used in a proportion of 0.01 to 5% by weight compared to the total weight of polymerisable monomers in the composition.

The polymerisable compositions according to the invention may also contain additives conventionally used in polymerisable compositions for moulding optical or ophthalmic articles, in particular spectacle glasses and lenses, in conventional proportions, for example inhibitors, colorants, UV

5 absorbers, perfumes, deodorants, antioxidants, anti-yellowing agents and photochromic compounds.

The compositions according to the invention may be polymerised thermally, photochemically or by a combination of the two methods.

The present invention will now be described in more detail in the

10 following examples. In the examples, except where otherwise stated, all percentages and parts are expressed by weight.

Examples 1 to 17

1) Preparation of the compositions

15 The polymerisable compositions listed in table I below were prepared by the following method :

The different components of the compositions were weighed in a room with controlled lighting, in smoked glass flasks.

PPG200DMA, monomer (I), and the co-monomers (II), a photoinitiator

20 and a UV absorber were mixed by stirring maintained for several minutes. A thermal initiator, stored at low temperature, was added as a final step (for reasons of stability).

2) Casting process

The compositions prepared as described above were cast into two-part

25 inorganic glass moulds previously cleaned with soda, assembled in parallel 2 mm apart with Barnier adhesive tape. The moulding was performed as follows :

• Taking up the composition in a sterile syringe (20 ml)

• Peeling back a little of the adhesive tape to create an opening

• Insertion of the syringe nozzle into the opening

30 • Injection of the composition into the mould

• Refixing the adhesive tape to seal the mould.

3) Photochemical prepolymerisation

The filled moulds were placed in a photochemical polymerisation oven composed of two U.V. PRIMA lamps (mercury lamps) positioned equidistantly

35 on either side of the moulds and each mould received from each lamp an illumination of about :

• 40 mW/m^2

• 125 mW/cm^2

The conversion of the (meth)acrylic double bonds as a function of the UV irradiation time was monitored by infrared measurements.

4) Thermal polymerisation and annealing

After polymerisation, the adhesive tape was removed and the assembly placed in an oven at 100°C for two hours to effect the polymerisation ; the glasses were then removed from the mould and checked under an arc lamp. A final annealing of two hours at 120°C completed the polymerisation and relaxed the residual stresses of the substrate obtained.

The properties of the substrates obtained are shown in table I.

The yellow index YI was measured according to ASTM standard D1925.

Colorability measurement (% Tv red)

The measurement given is the value of the transmission measured in the visible of a lens of 2 mm thickness at the centre coloured by soaking in an aqueous bath at 94°C in which the red pigment "disperse Red 13" from Eastman Kodak had been dispersed.

The measurement of Tg was performed by DMA (dynamic mechanical analysis) on a flat sample 5.2 cm x 1 cm x 2 mm (thick).

The test was performed by 3 point bending.

Tg corresponds to the maximum of the ratio

$$\frac{E'' \; (\; loss \; modulus \;)}{E' \; (conservation \; modulus)}$$

TABLE I

EXAMPLE No.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
PPG 200 dimethacrylate Parts by weight	95	90	85	95	90	85	80	75	95	90	80	75	70	90	80	90	80
Urethane co-monomer Parts by weight																	
U4H	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CN965	-	10	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CN934	-	-	-	5	10	15	20	25	5	10	15	20	25	-	-	-	-
Ebecryl® 270	-	-	-	-	-	-	-	-	-	-	-	-	-	10	20	-	-
Ebecryl® 8800	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	20
Photoinitiator CGI 1850 (%)	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Thermal initiator tBPEH (%)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
UV absorber UV 5411 (%)	0.08	0.08	0.08	0.08	0.08	0.08-	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
n_e	1.493	1.495	1.494	1.493	1.495	1.494	1.494	1.494	1.494	1.494	1.495	1.494	1.494	1.493	1.493	1.495	1.496
ν_e^d	58	55	57	55	55	57	55	56	55	54	55	55	55	55	56	54	55
YI (2 mm)	1.8	1.9	1.8	1.9	2.0	2.5	3.8	3.8	1.7	1.7	1.7	-	1.8	1.8	1.5	2.1	2.7
%Tv red	72	76	80	69	64	40	35	32	63	58	45	39	33	56	49	55	50
Tg (°C)	-	-	140	-	135	130	-	115	-	-	116	108	104	-	-	-	120
E'25°C (MPa)	-	-	2200	-	2600	1900	-	1800	-	-	2050	1920	1780	-	-	-	2200
E'100°C (MPa)	-	-	750	-	1100	490	-	380	-	-	490	380	280	-	-	-	495

The impact strength was determined on 21 lenses of -2 dioptres, with thickness at centre 1.07 mm, obtained by polymerisation of the composition of example 12, as described above. In the test, balls were dropped with increasing energy on the centre of the lens until the lens starred or broke. The average breaking energy was then calculated.

The average breaking energy was 1900 ± 500 mJ.

Examples 18 to 30

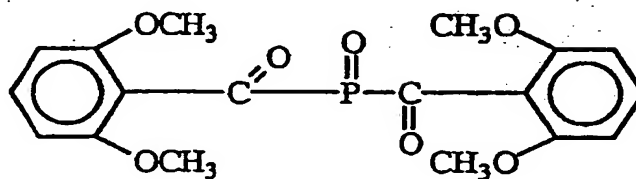The polymerisable compositions of table II below were prepared as before.

The properties of the substrates obtained are given in table II.

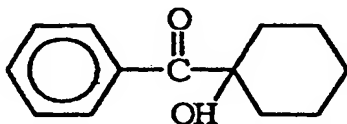These properties were determined as for the previous examples.

TABLE II

	EXAMPLE No.												
	18	19	20	21	22	23	24	25	26	27	28	29	30
PPG 200 dimethacrylate - Parts by weight	63	56	49	54	48	40	30	63	54	54	54	54	54
CD6440P (Cray Valley) - Parts by weight	27	24	21	36	32	40	30	27	36	36	36	36	36
Urethane co-monomer - Parts by weight													
PLEX® 6610	10	20	30	10	20	20	40	-	-	-	-	-	-
SR290	-	-	-	-	-	-	-	10	10	-	-	-	25
U4H	-	-	-	-	-	-	-	-	-	10	-	-	-
CN934	-	-	-	-	-	-	-	-	-	-	10	-	-
CN964	-	-	-	-	-	-	-	-	-	-	-	10	-
SR368	-	-	-	-	-	-	-	-	-	-	-	-	10
% by weight monomer (I)/total monomers	75.1	66.8	58.4	70.2	62.4	58	43.5	75.1	70.2	70.2	70.2	70.2	70.2
Photoinitiator CGI 1850 (%)	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Thermal initiator tBPEH (%)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
UV absorber UV 5411 (%)	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
n_e	1.493	1.496	1.498	1.493	1.495	1.490	1.500	1.495	1.495	1.494	1.491	1.492	1.494
v_e	55	56	56	56	55	55	56	54	56	55	54	57	56
d	1.13	1.15	1.15	1.13	1.14	1.13	1.13	1.15	1.15	1.14	1.13	1.13	1.15
YI (2 mm)	1.5	1.2	1.2	1.5	1.5	1.5	1.2	1.6	1.7	-	1.4	1.5	1.4
%Tv red	45	49	49	45	45	42	51	43	40	41	39	39	46
Tg (°C)	102	-	118	100	104	84	114	106	109	-	88	88	-
E'25°C (MPa)	2000	-	2200	1650	1870	1350	2290	1770	1600	-	1330	1430	-
E'100°C (MPa)	350	-	420	285	320	170	359	486	400	-	180	196	-

CGI1850 = photoinitiator from the company CIBA GEIGY composed of a mixture (in mass ratio 50/50) of

$$\text{(OCH}_3\text{-substituted benzoyl)}-C(=O)-P(=O)-C(=O)-\text{(CH}_3\text{O-substituted benzoyl)}$$

5   and of

$$\text{C}_6\text{H}_5-C(=O)-C(OH)(\text{cyclohexyl})$$

| tBPEH | = | tert-butyl peroxy-2-ethylhexanoate |
| UV 5411 | = | 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole from the company American Cyanamid |

10

n_e	=	refractive index
v_e	=	Abbe number
d	=	density
Yi	=	yellow index
E'25 \} E'100	=	elastic moduli at 25°C and 100°C respectively

15

The viscosities were determined on 250 ml samples at 25°C by means of a BROOKFIELD model DV2 viscometer at shearing speeds varying from 6 to 60 rpm (mobile No. 61 or No. 62). The mobile No. 61 was used at a shearing
20   speed of 12 rpm.

The refractive indexes (λ = 546 nm) and the Abbe numbers were determined at 25°C using a BELLINGHAM-STANLEY LIMITED ABBE 60/TR with different lamps (sodium, mercury and cadmium) at light sources.

The DMA analyses were performed with a Rheometrics Solid Analyser
25   RSA II on 52 x 10 x 2 mm samples, at a frequency of 1 Hz and over a temperature range of -50°C to 170°C at 2°C /minute.

The impact strength of the lenses (power -2 dioptres and thickness at centre 1.10 mm) was determined by polymerisation of a reference composition CD6440P/PPG 200 DMA 30/70 under the conditions described above. The
30   average breaking strength was 1200 ± 900 mJ and two lenses out of 18 failed the test.

The impact strength of 20 lenses of power -2 dioptres and thickness at centre 1.09 mm obtained by polymerisation of the composition of example 22 was also determined. The average breaking strength was 1200 ± 800 mJ and 1 lens out of 20 failed the test.

5   The impact strength test consisted of dropping balls with increasing energy on the centre of the lens until the lens broke (breakage or starring). The average breaking energy was thus determined.

A water absorption test was performed on the lenses of examples 6 and 12. The lenses, dried in an oven, were weighed, then immersed in water at 10   90°C for 30 minutes. The lenses were recovered, then reweighed.

The water absorption level was determined as :

$$T_{water} = \frac{\text{Weight after water treatment - Initial weight}}{\text{Initial weight}} \times 100$$

15

The lenses of examples 6 and 12 gave figures of 0.59 and 0.74% respectively.

CD6440P is a mixture of several monomers corresponding to the general 20   formula (I) whose repeating unit is

$$-(CH_2 - CH - O)_{\overline{m2}}$$
$$\overset{|}{CH_3}$$
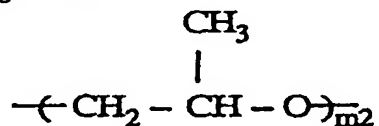
with m_2 being an integer with values from 3 to 10 according to the following mass ratios :

$m_2 = 3$	2%
$m_2 = 4$	8%
$m_2 = 5$	14%
$m_2 = 6$	20%
$m_2 = 7$	27%
$m_2 = 8$	19%
$m_2 = 9$	9%
$m_2 = 10$	1%.

25

30